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ELECTRONIC SUPPORTING INFORMATION

Supramolecular and Electrocatalytic Properties of Two New Structurally Diverse Tertiary Phosphane Appended Nickel(II) and Copper(I) Thiosquarates

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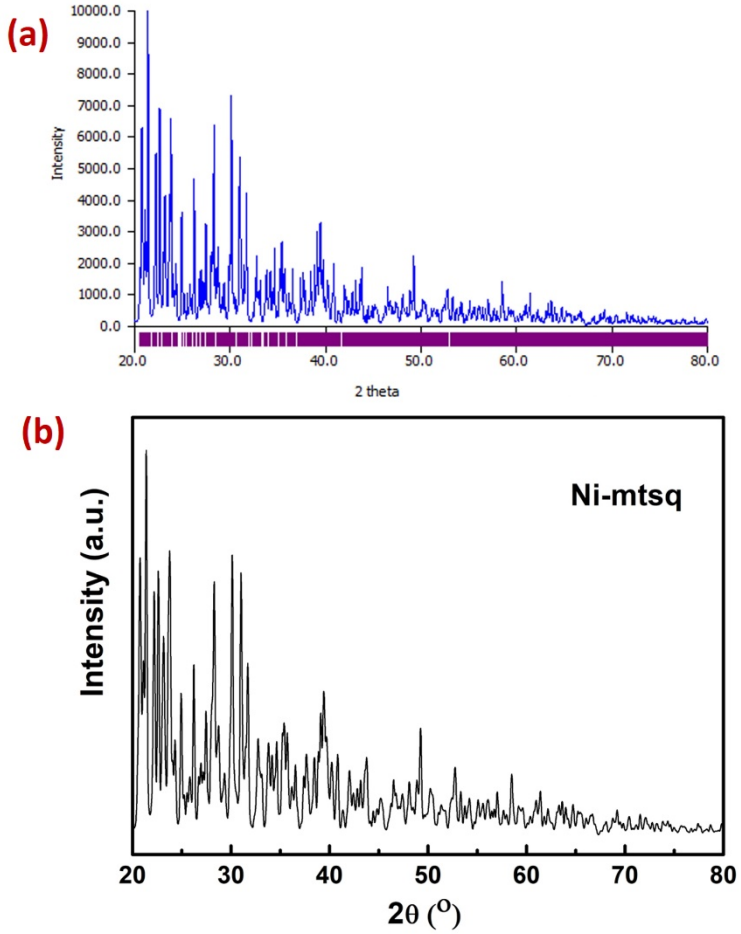

Fig. S1 (a) Simulated and (b) experimental PXRD plots for **Ni-mtsq**.

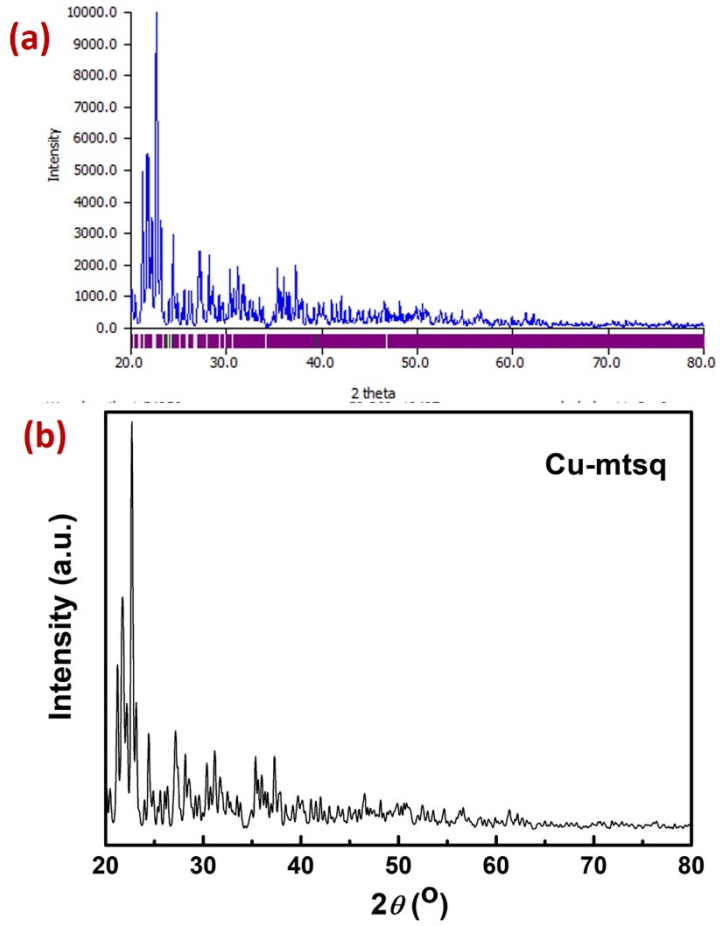

Fig. S2 (a) Simulated and (b) experimental PXRD plots for **Cu-mtsq**.

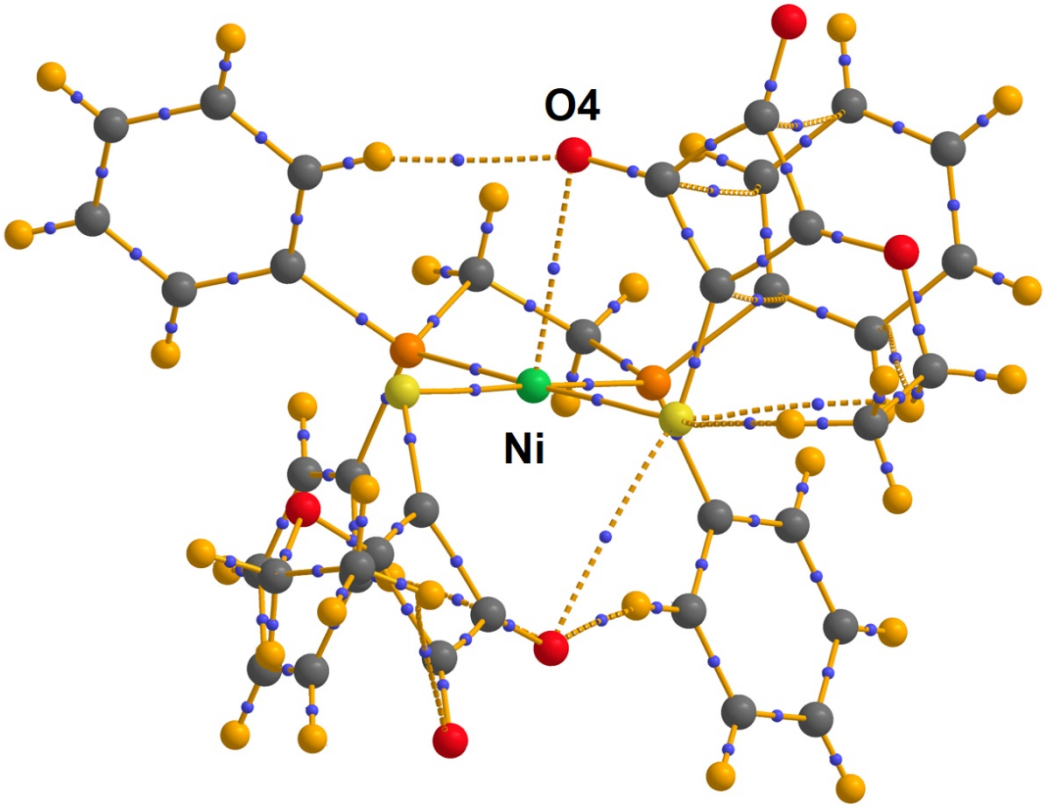

Fig. S3 Molecular graph for **Ni-mtsq** displaying intramolecular Ni···O interaction.

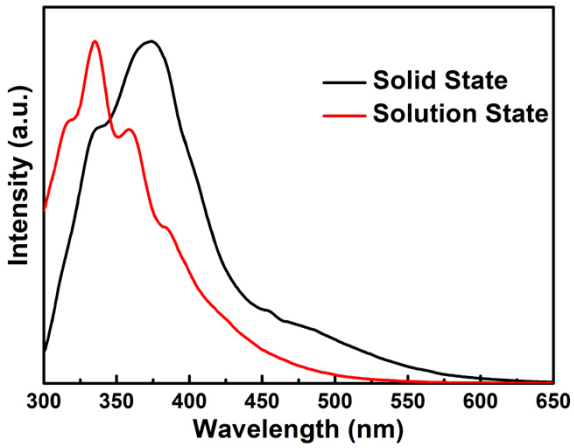

Fig. S4 Emission spectra for **Cu-mtsq** recorded in 1×10^{-3} M chloroform solution and in solid state.

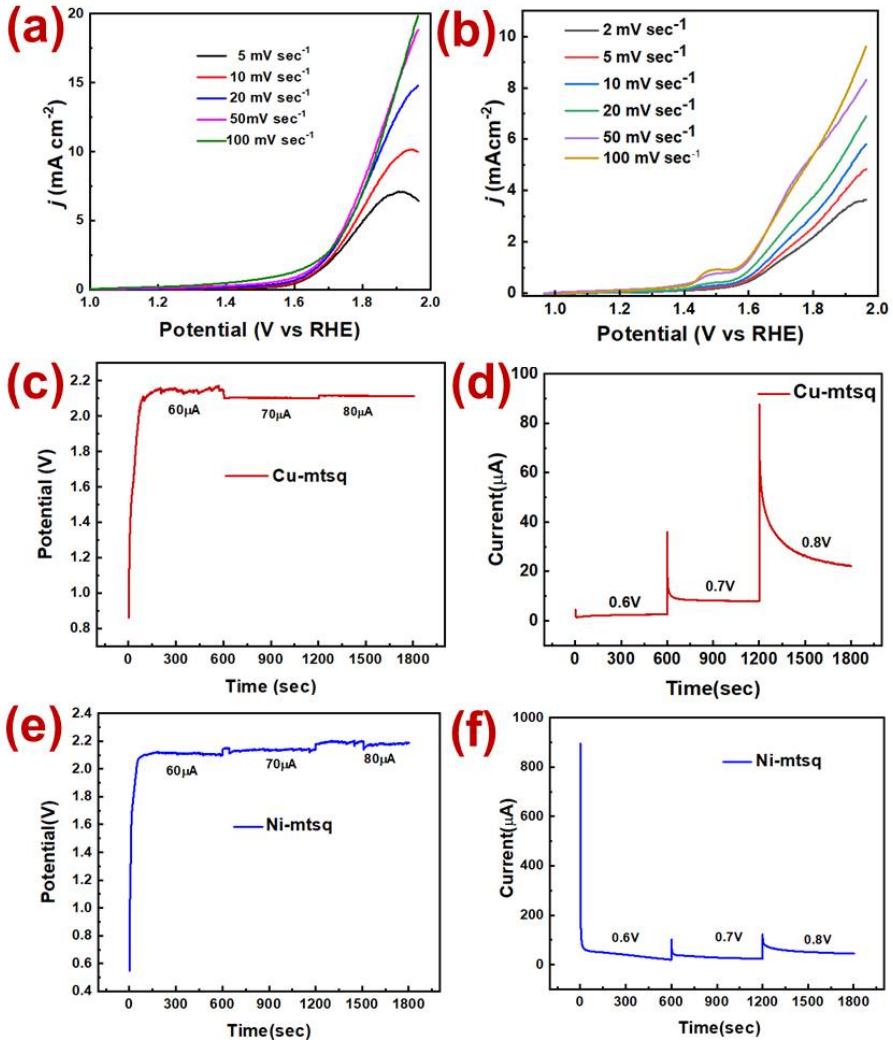

Fig. S5 (a) and (b) Linear Sweep Voltammetry plots of **Cu-mtsq** and **Ni-mtsq** recorded at different scan rates (c) and (e) Chronopotentiometry plots (d) and (f) Chronoamperometry plots for **Cu-mtsq** and **Ni-mtsq** in 0.1 M KOH.

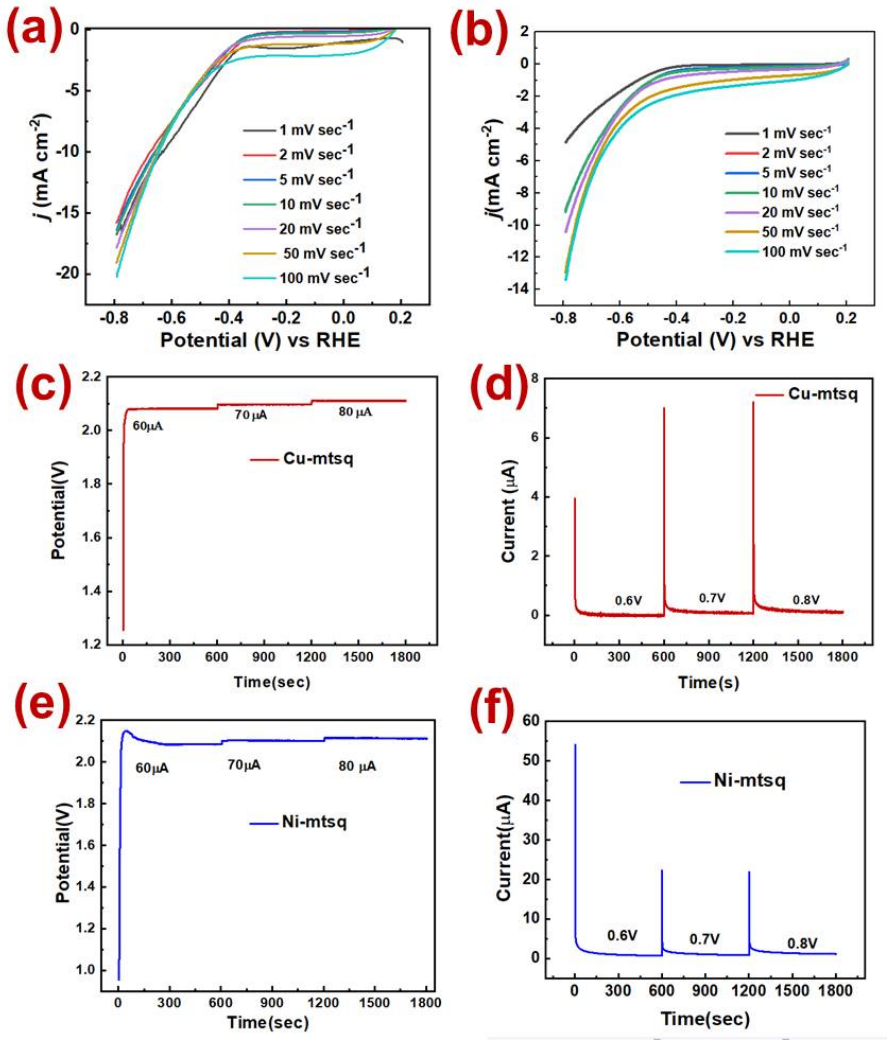

Fig. S6 (a) and (b) Linear Sweep Voltammograms at different scan rates; (c) and (e) Chronopotentiometry and Chronoamperometry plots of **Cu-mtsq** and **Ni-mtsq** (d) and (f) in 0.5 M H_2SO_4.

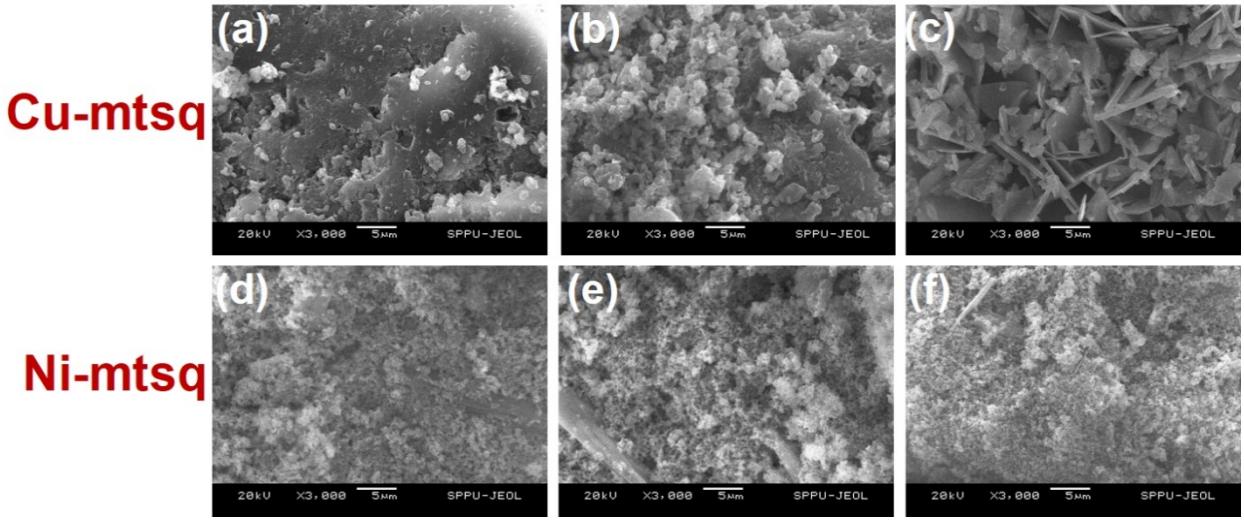

Fig. S7 FESEM images for (a) and (d) Pure **Cu-mtsq** and **Ni-mtsq**; (b) and (e) **Cu-mtsq** and **Ni-mtsq** after OER electrocatalysis in 0.1 M KOH; (c) and (f) **Cu-mtsq** and **Ni-mtsq** after HER electrocatalysis in 0.5 M H_2SO_4.

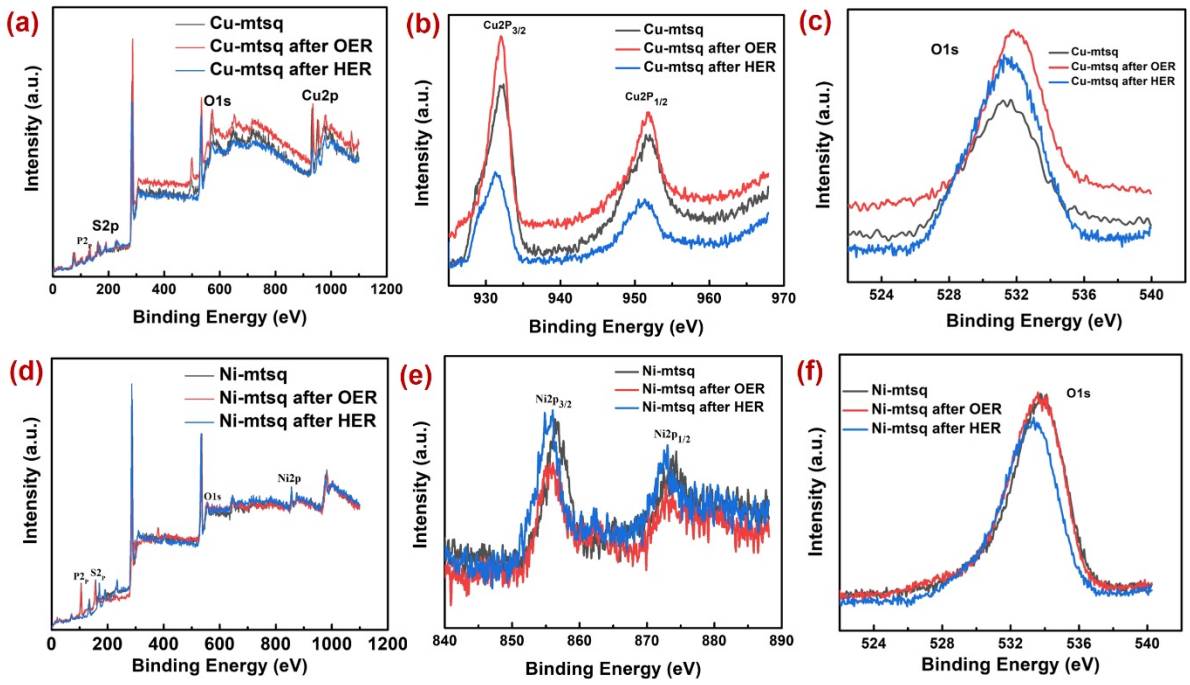

Fig. S8 (a), (d) X-ray photoemission spectroscopy survey spectra taken on **Cu-mtsq** and **Ni-mtsq** before and after OER in 0.1 M KOH and after HER in 0.5 M H_2SO_4; (b) XPS plot for Cu 2p, peak fitting, and it indicated that Cu has more than one oxidation i.e., Cu^{2+} and Cu^{+} (c) XPS plot for O1s for **Cu-mtsq**; (e) XPS data for Ni 2p, peak fitting indicating Ni^{2+} (c) XPS plot for O1s for **Ni-mtsq**.

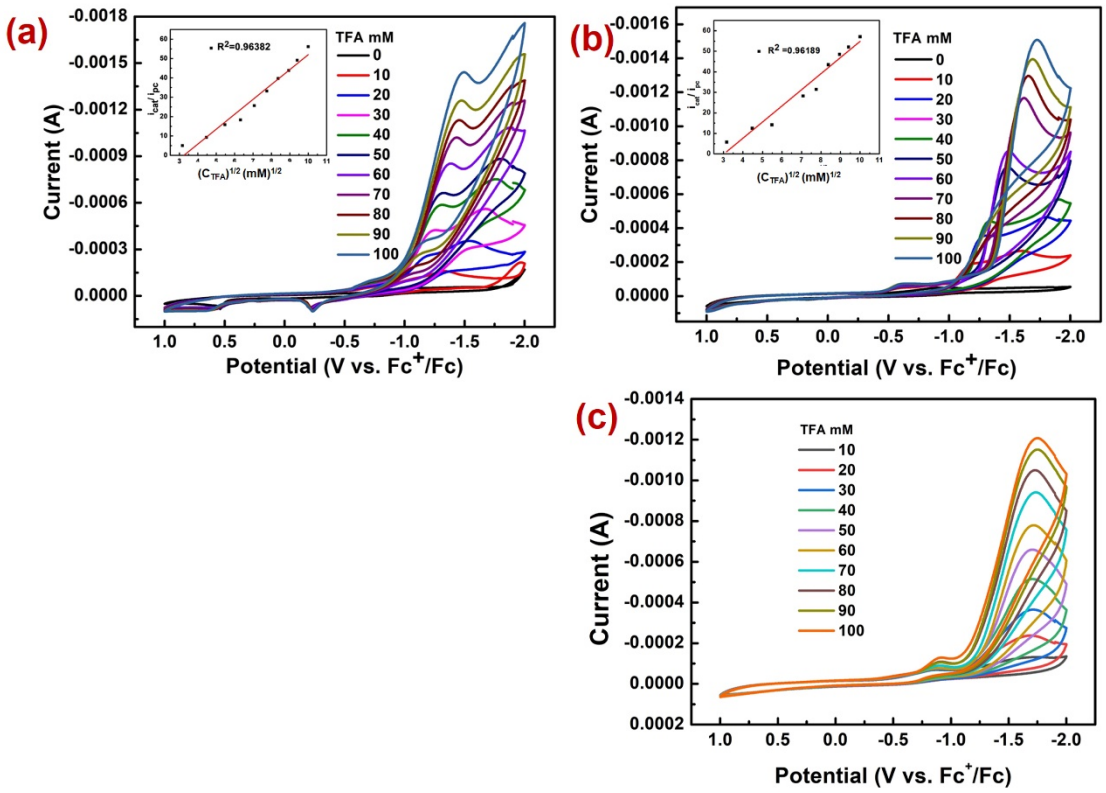

Fig. S9 Cyclic voltammograms for (a) **Cu-mtsq** and (b) **Ni-mtsq** in presence of TFA (0-100 mM) in acetonitrile:dichloromethane (2:3 V/V) mixture. Inset: Plots of the normalized plateau current (i_{cat}/i_{pc}) against the square root of the concentration of concentration of TFA for both the complexes (1 mM). (c) Cyclic voltammograms under controlled conditions without the adding **Cu-mtsq** and **Ni-mtsq**. Conditions: 0.1 M n-Bu_4NPF_6 as supporting electrolyte, glassy carbon working electrode (3 mm diameter); platinum wire counter electrode; $Ag/AgNO_3$ reference electrode; potential vs. Fc^+/Fc; 100 $mV.s^{-1}$ scan rate.

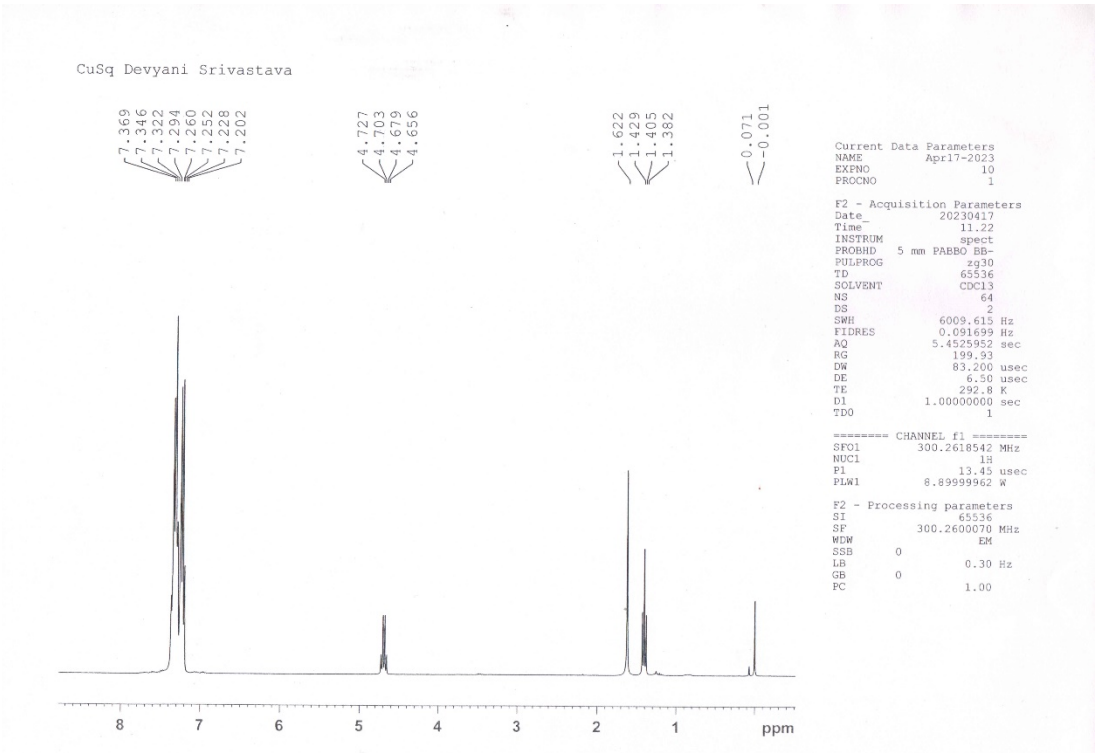

Fig. S10 ^{1}H NMR spectrum for **Cu-mtsq.**

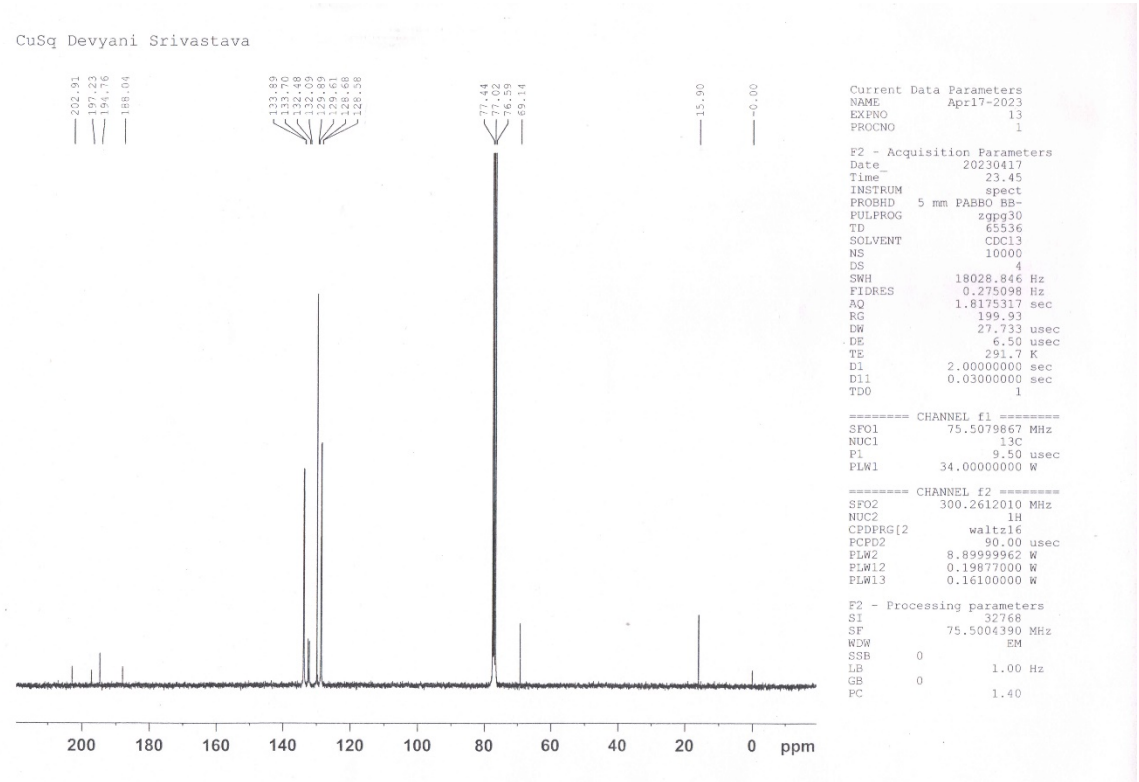

Fig. S11 ^{13}C NMR spectrum for **Cu-mtsq.**

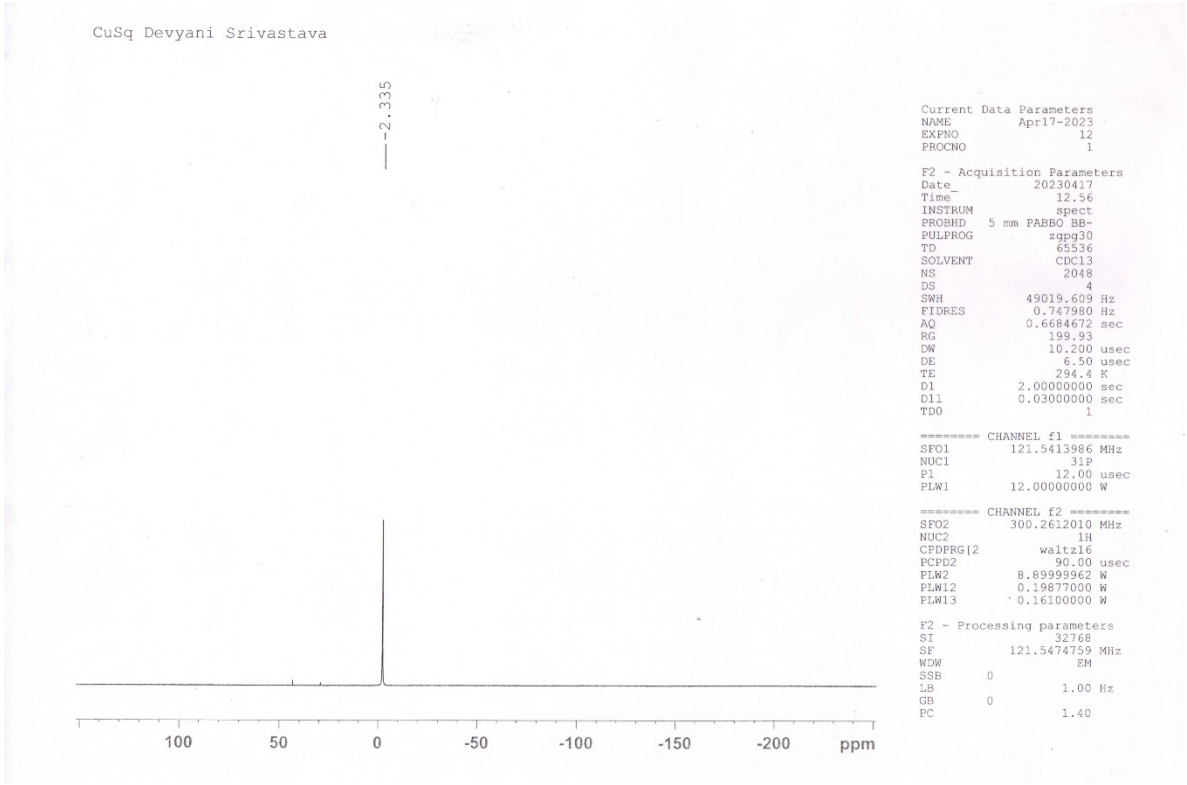

Fig. S12 ^{31}P NMR spectrum for **Cu-mtsq.**

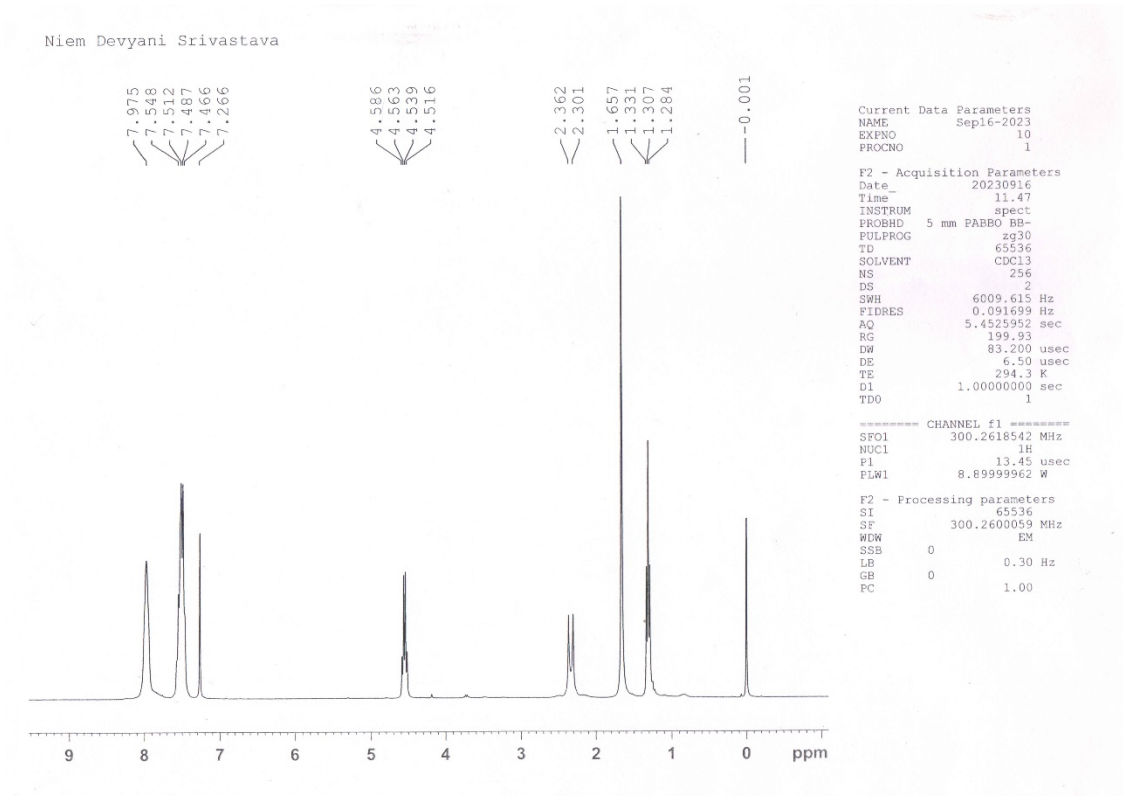

Fig. S13 ^{1}H NMR spectrum for **Ni-mtsq.**

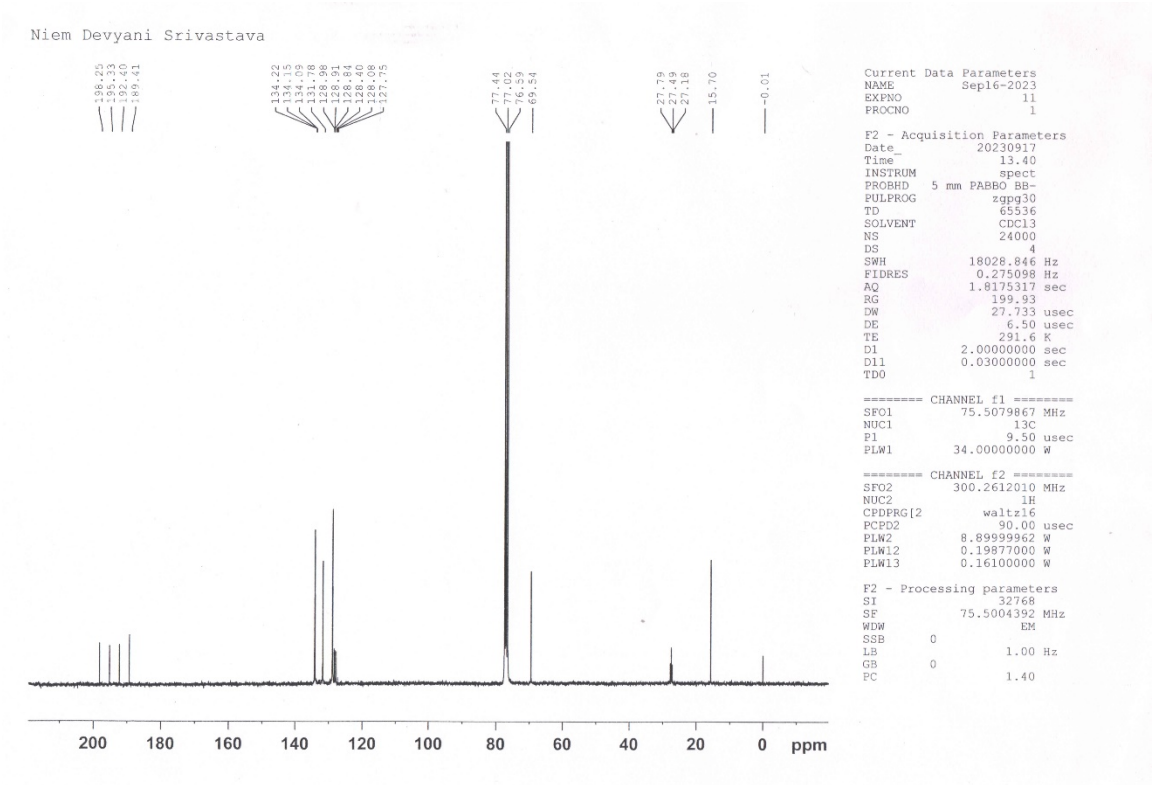

Fig. S14 ^{13}C NMR spectrum for **Ni-mtsq.**

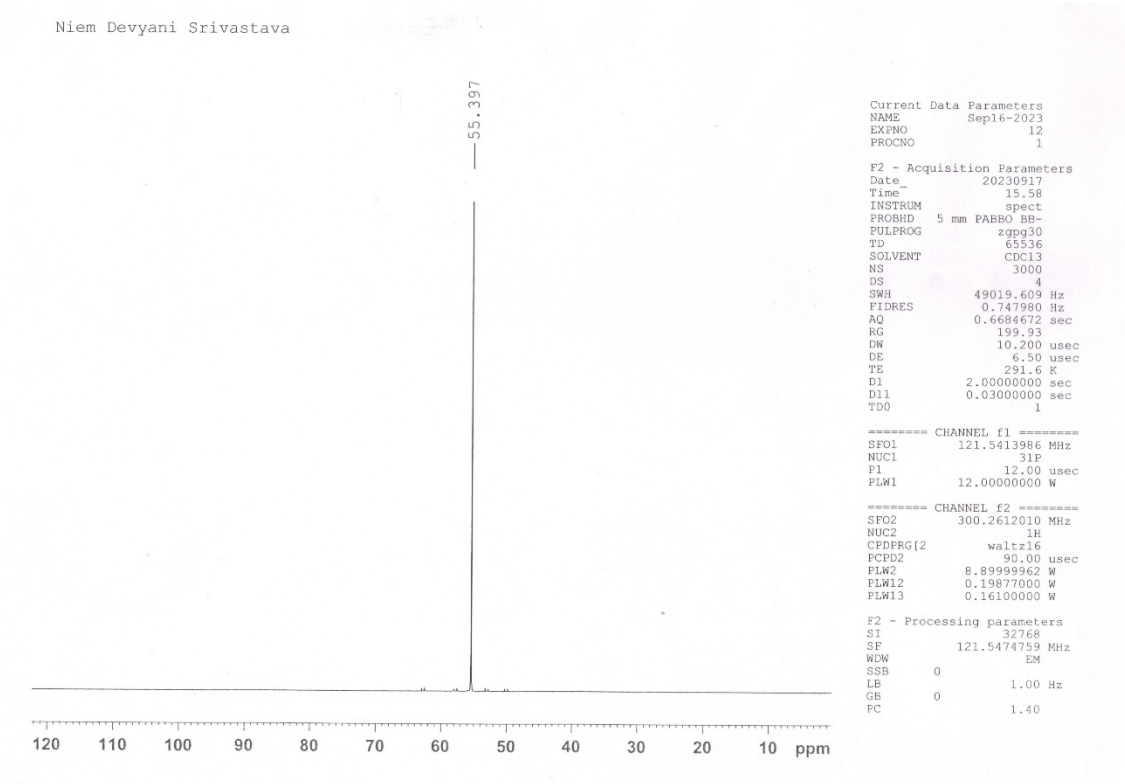

Fig. S15 ^{31}P NMR spectrum for **Ni-mtsq.**

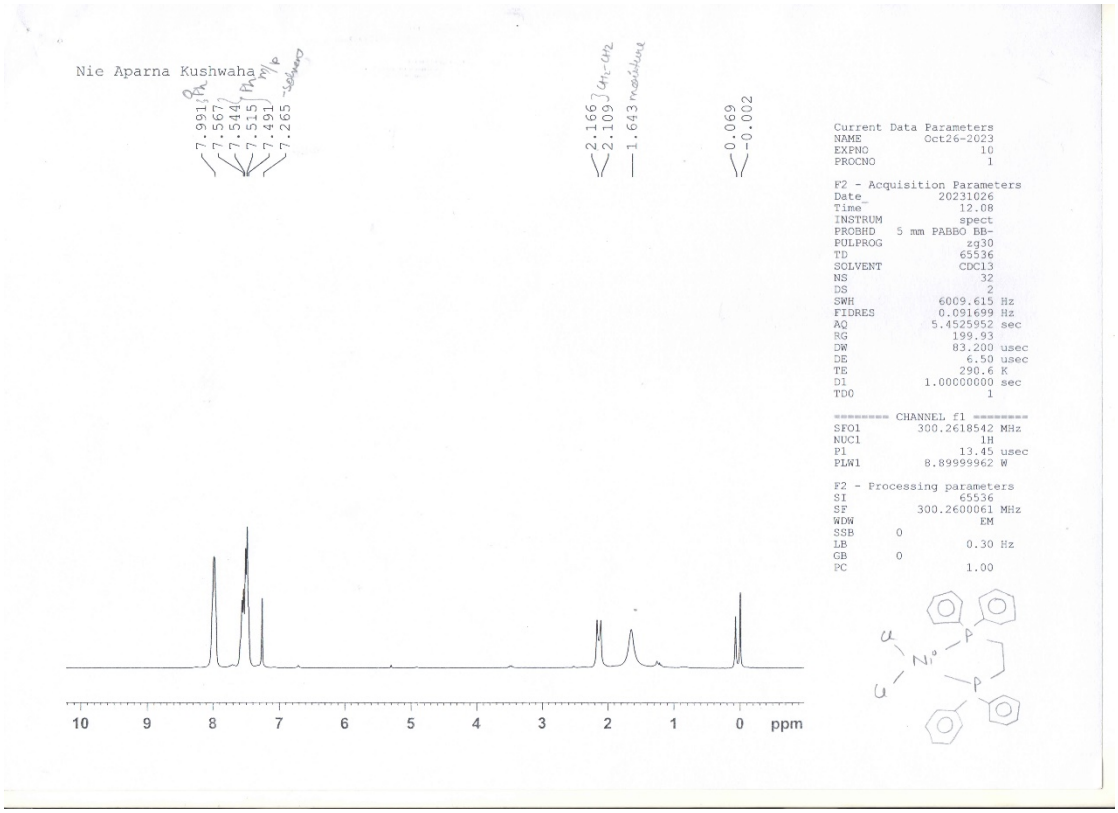

Fig. S16 ^{1}H NMR spectrum for **NidppeCl$_2$.**

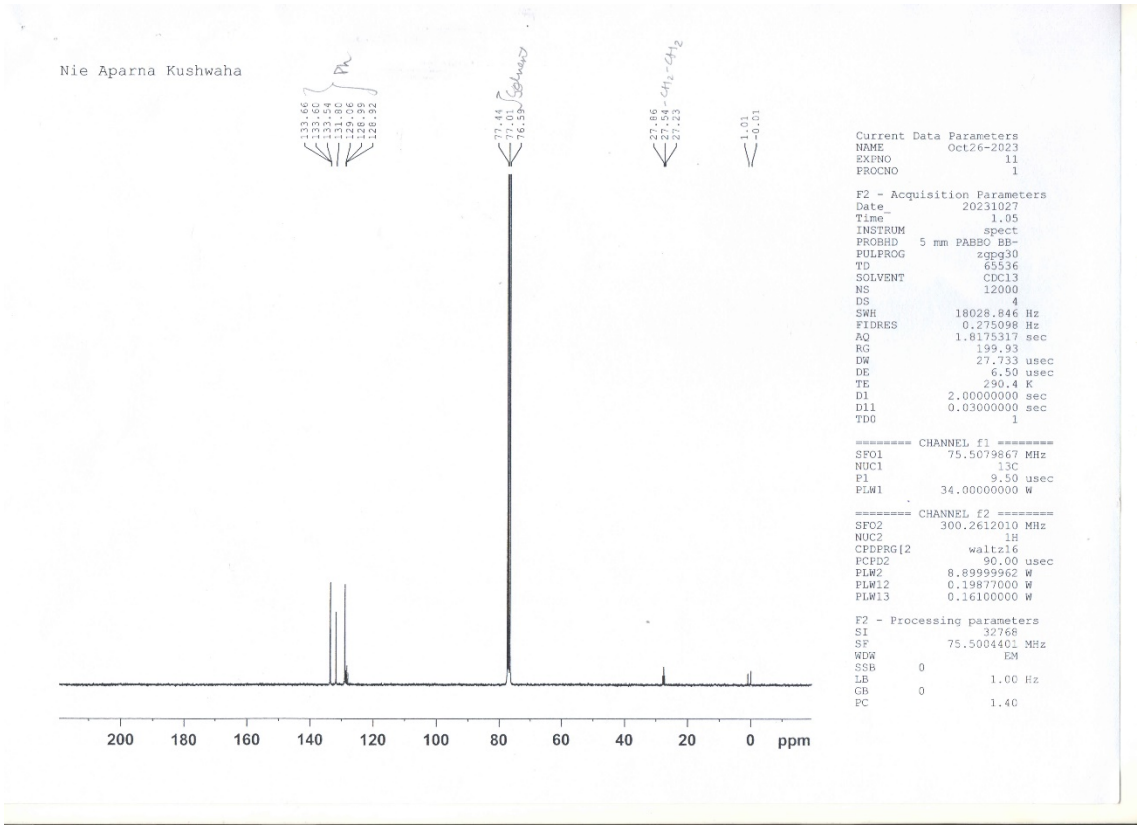

Fig. S17 ^{13}C NMR spectrum for **NidppeCl$_2$.**

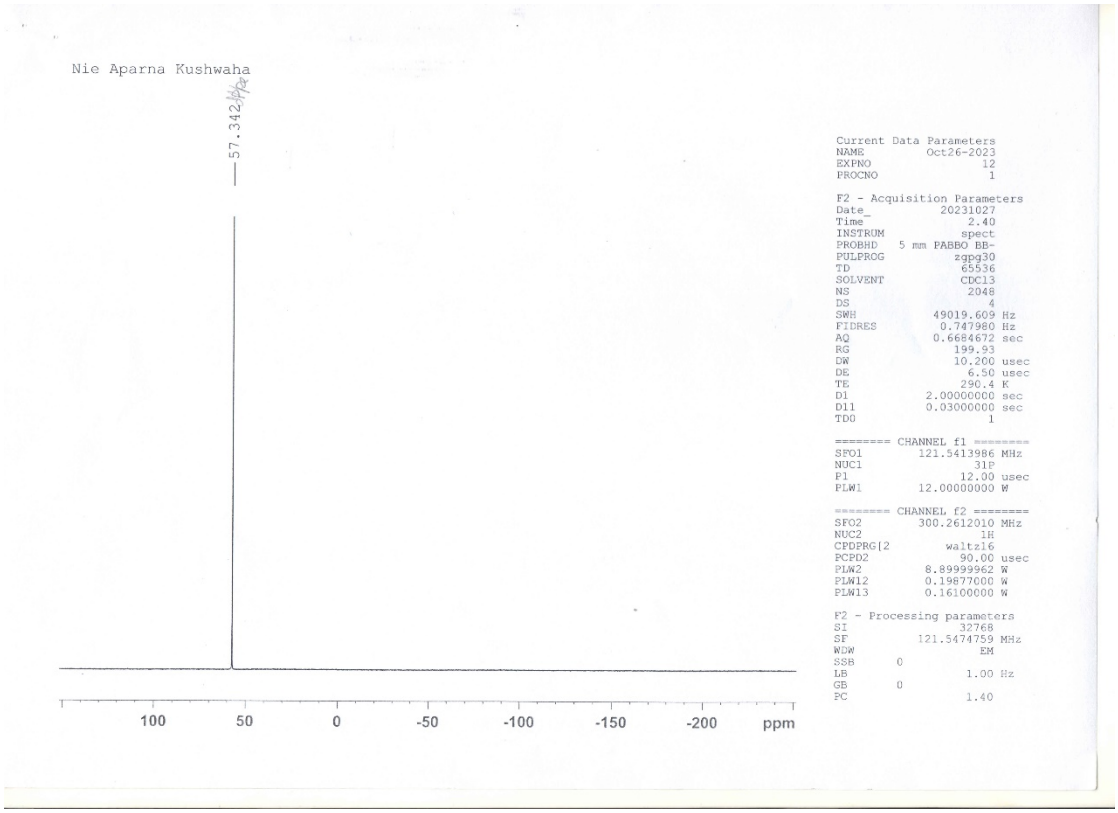

Fig. S18 ^{31}P NMR spectrum for **$NidppeCl_2$.**

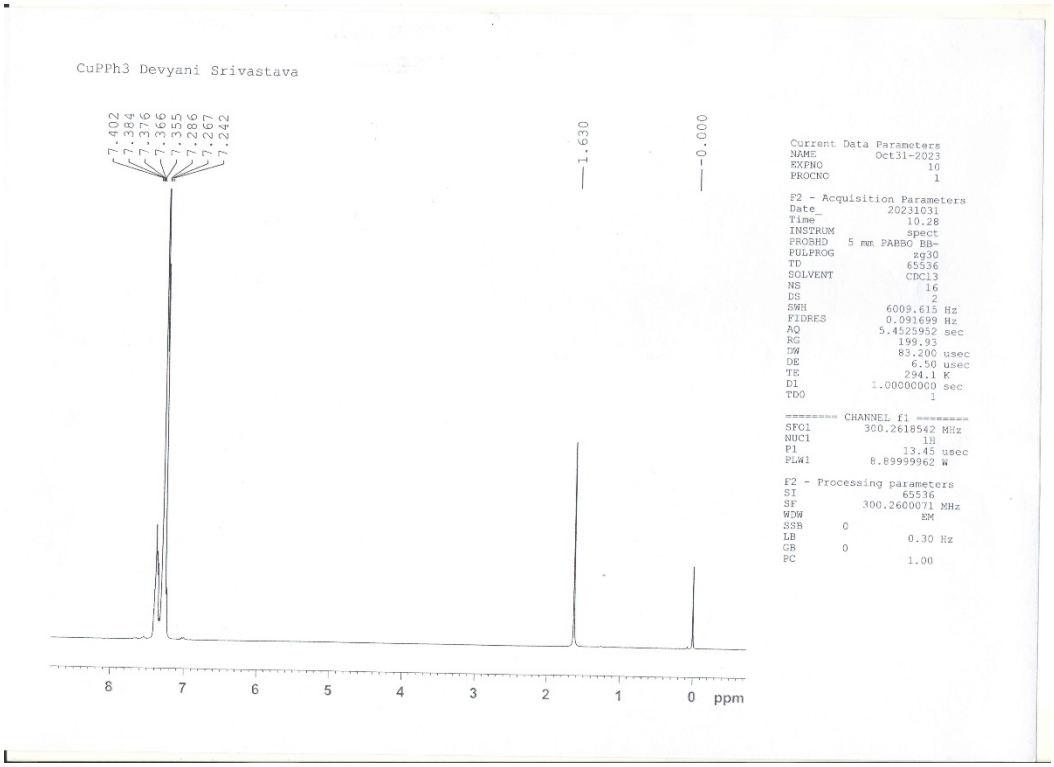

Fig. S19 ^{1}H NMR spectrum for **$Cu(PPh_3)_2NO_3$.**

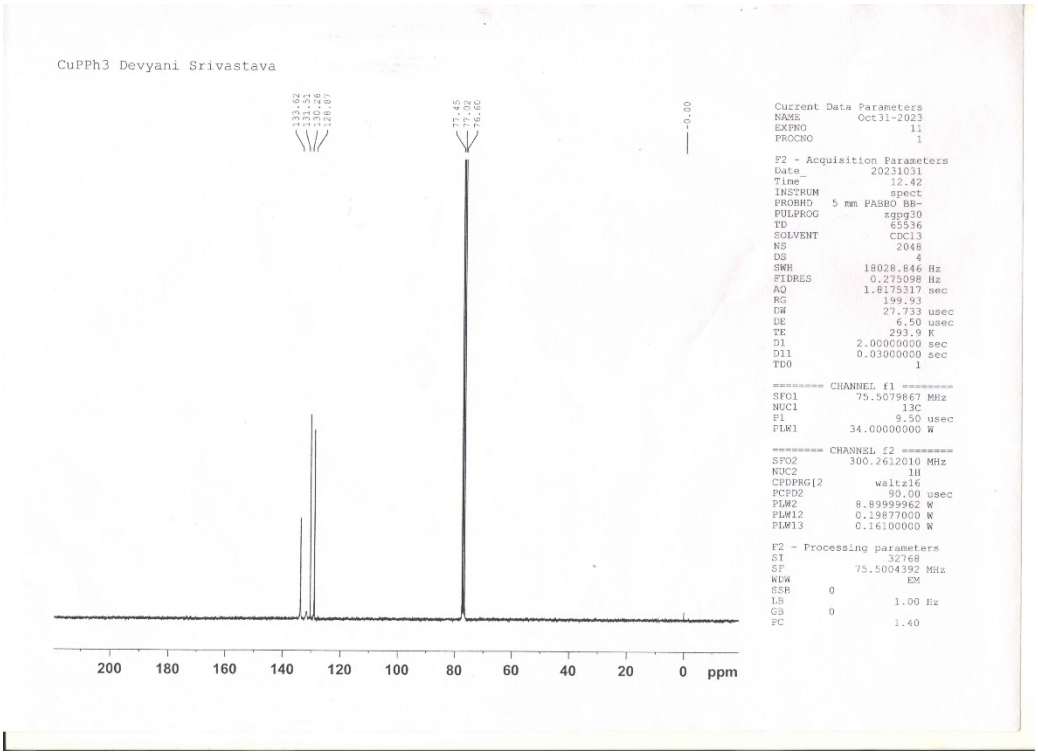

Fig. S20 ^{13}C NMR spectrum for **$Cu(PPh_3)_2NO_3$.**

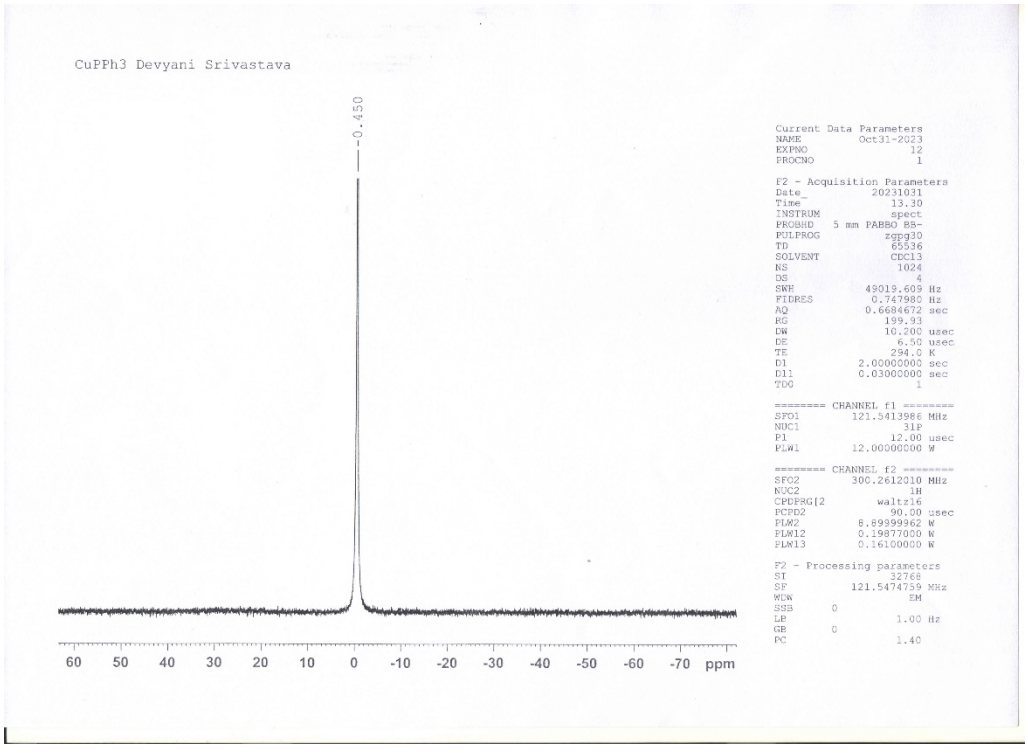

Fig. S21 ^{31}P NMR spectrum for **$Cu(PPh_3)_2NO_3$.**

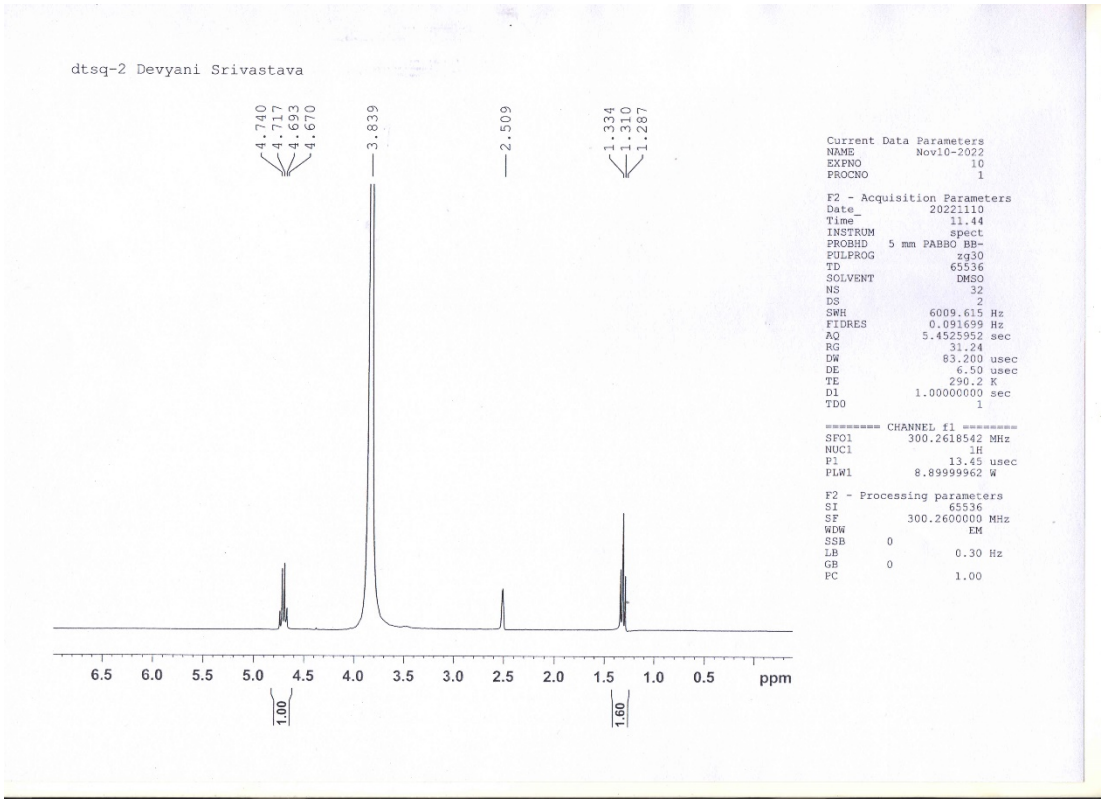

Fig. S22 ^{1}H NMR spectrum for **Namtsq.**

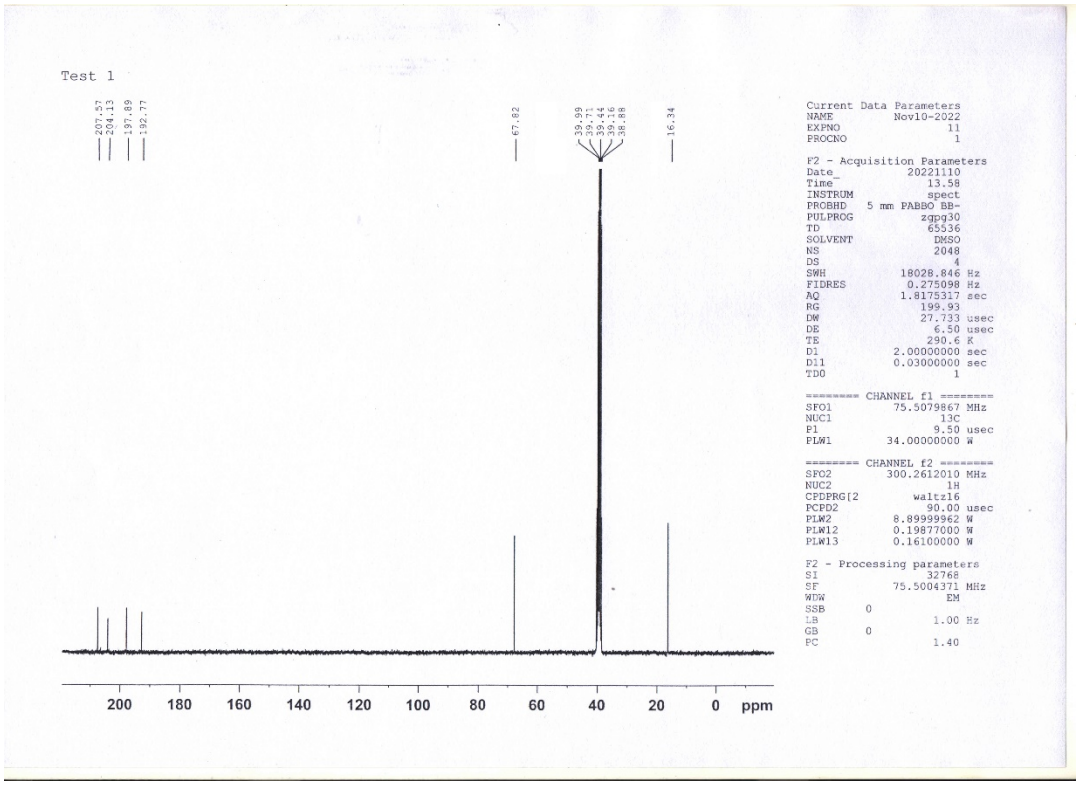

Fig. S23 ^{13}C NMR spectrum for **Namtsq.**

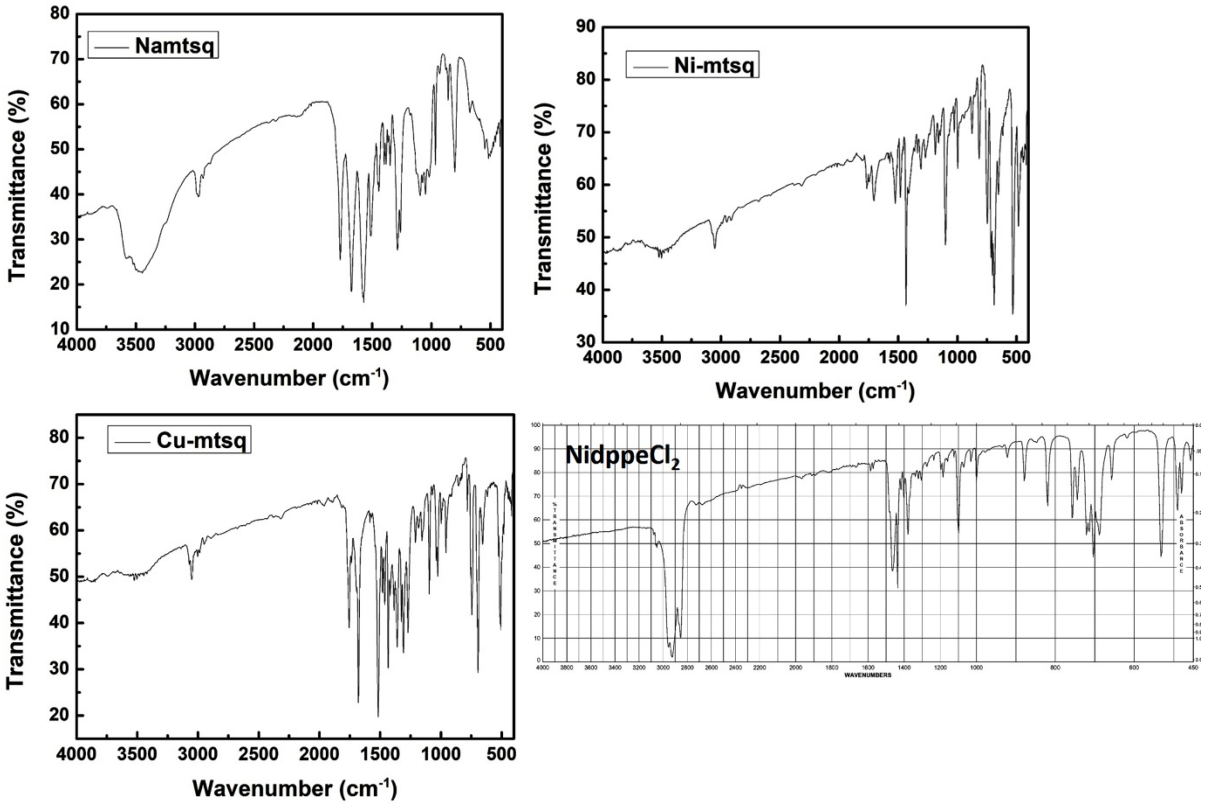

Fig. S24 FTIR spectra for the Namtsq ligand, Ni-mtsq, Cu-mtsq and $NidppeCl_2$.

Table S1 Overview of the OER catalytic activity of Nickel and Copper based catalysts

SAMPLES	ONSET (V)	η(current density) mV	TAFEL SLOP	REFERENCE
GCE/Nf/$[Ni(thpch)_3]^{2+}$		1.68(10)	41.5	1
1		-	128.0	2
1-GO	1.691	1.76(0.5)	100.6	
1-rGO	1.625	1.71(0.5)	76.9	
1-g-C_3N_4	1.630		126.4	
GC_{rde}/Nf-2	1.52	1.58(10)		3
[(LGly-Cu)4]		0.62(1)		4
[(LGlu-Cu)4]		0.76(1)		
Cu(pyalk)2				5
Cu-mtsq	1.55	1.754	228	This work
Ni-mtsq	1.54	1.778		This work

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